2003-0099523

(Translation)

[DOCUMENT NAME] Specification

[TITLE OF THE INVENTION] Negative electrode active material and non-aqueous electrolyte rechargeable battery using the same

[CLAIMS]

[Claim 1] A negative electrode active material for a non-aqueous electrolyte rechargeable battery capable of adsorbing/desorbing lithium comprising: an inner layer comprising at least one selected from the group consisting of Si, Sn, an alloy containing Si and an alloy containing Sn; and a surface layer comprising silicon oxide or tin oxide of 0.2 to 1,000 nm in thickness formed on said inner layer.

[Claim 2] The negative electrode active material for a non-aqueous electrolyte rechargeable battery in accordance with claim 1, wherein said alloy comprises Si or Sn, and at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe.

[Claim 3] The negative electrode active material for a non-aqueous electrolyte rechargeable battery in accordance with claim 1, wherein said alloy comprises at least an Si phase or an Sn phase and an alloy phase containing at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe.

[Claim 4] The negative electrode active material for

a non-aqueous electrolyte rechargeable battery in accordance with any one of claims 1 to 3, which is in the form of a thin film or a powder.

[Claim 5] The negative electrode active material for a non-aqueous electrolyte rechargeable battery in accordance with any one of claims 1 to 4 including an amorphous Si phase.

[Claim 6] The negative electrode active material for a non-aqueous electrolyte rechargeable battery comprising the negative electrode active material in accordance with any one of claims 1 to 5.

[DETAILED DESCRITION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a negative electrode active material for a non-aqueous electrolyte rechargeable battery, and more specifically relates to a non-aqueous electrolyte rechargeable battery having high capacity, and excellent cycle life characteristic and high-temperature storage characteristic.

[0002]

[Prior Art]

A lithium rechargeable battery has conventionally been used as a power source for mobile telecommunication equipment and portable electronic equipment. The lithium secondary battery exhibits higher electromotive force and higher energy density than alkaline storage batteries such as

a nickel-cadmium storage battery and a nickel metal-hydride

storage battery and utilizes lithium metal or graphite powder

as a negative electrode material.

[0003]

However, when the lithium metal is used as the

negative electrode material of the lithium rechargeable

battery, dendrites are deposited on the negative electrode in

a charging state. The dendrites grow through repeated charge

and discharge and penetrate a separator, which may possibly

cause internal short circuit. Correspondingly, the cycle life

may possibly decrease.

On the other hand, when the graphite powder is used

as the negative electrode material of the lithium rechargeable

battery, the theoretical capacity of the graphite powder (372

mAh/g) is about 10 % of that of elemental lithium metal.

Therefore, the graphite powder is disadvantageous in that it

cannot meet the growing demand for higher energy density.

[0004]

Under these circumstances, in recent years, attempts

have been made to use other materials having higher

theoretical capacity as novel negative electrode materials,

e.g., silicon (theoretical capacity: 4199 mAh/g), tin

(theoretical capacity: 993 mAh/g) and an alloy containing

these elements.

For example, Patent Document 1 discloses a negative

electrode material represented by $M_{100-x}Si_x$ (where M is Ni, Fe,

Co or Mn and x (at%) $\geq$ 50).

[0005]

Further, the Publication also discloses how to produce the negative electrode material. First, M and Si are weighed to have a predetermined molar ratio (1-x):x and melted by high-frequency induction melting process in atmospheric air to obtain a molten alloy. This molten alloy is quenched by a single roll process or the like for solidification to give an alloy mass of $M_{1-x}Si_x$. Then, the alloy mass is pulverized into a fine powder using a jet mill to obtain an alloy powder as the negative electrode material.

[0006]

[Patent Document 1]

Japanese Laid-Open Patent Publication No. Hei10-294112

[0007]

[Problem That the Invention Is to Solve]

However, the inventors' analysis has found that the above material is high in capacity but unsatisfactory in cycle life characteristic.

According to a charge/discharge test of a battery similar to that of Example 3 of the Patent Document 1, the initial battery capacity was as high as about 1300 mAh/cc. However, after the 100th charge/discharge cycle, the battery capacity was reduced to 30% of the capacity at the first cycle. Therefore, sufficient cycle life characteristic was not

obtained.

[0008]

A cause of the insufficient cycle life characteristic is considered as follows.

During the preparation of the molten alloy by high-frequency induction melting process in atmospheric air, oxygen becomes mixed therein to form silicon oxide on the alloy surface. Since the resistivity of silicon oxide is as high as 10^{12} $\Omega \cdot m$ ("Latest Handbook of Oxide", Moscow Metallurgy), Li ions are not smoothly adsorbed to and desorbed from the alloy surface in a charge/discharge reaction. Thereby, the reaction resistance is prone to increase.

[0009]

In fact, the presence of silicon oxide was actually observed on the alloy surface by X-ray photoelectron spectroscopy (XPS). A thickness of silicon oxide was about 1,100 nm, which increased up to about 1,300 nm after the 100th cycle. The precise mechanism of the increase in thickness of silicon oxide through the repeated charge and discharge is unknown. However, due to the presence of silicon oxide having high reaction resistance, a side reaction is prone to occur between oxygen atoms in the electrolyte and the alloy containing silicon, as well as the electrochemical reaction between the alloy and the Li ions. For that reason, it is presumed that silicon oxide increased in thickness through the repeated charge and discharge.

[0010]

Therefore, the increase in thickness of this silicon oxide brings about an increase in reaction resistance, which presumably results in the unsatisfactory cycle life characteristic.

According to a close study on this matter, the inventors of the present invention have found it effective at solving the above problem to limit the thickness of silicon oxide formed on the surface of the alloy.

[0011]

Thus, to solve the conventional problems described above, the present invention intends to provide a negative electrode active material for a non-aqueous electrolyte rechargeable battery which adsorbs a large amount of lithium and has reduced reaction resistance. Further, with the use of the negative electrode active material, the present invention intends to provide a non-aqueous electrolyte rechargeable battery having high capacity, and excellent cycle life characteristic and high-temperature storage characteristic.

[0012]

[Means for Solving the Problem]

A negative electrode active material for a non-aqueous electrolyte rechargeable battery of the present invention is capable of adsorbing and desorbing lithium and comprises: an inner layer comprising at least one selected from the group consisting of Si, Sn, an alloy containing Si

and an alloy containing Sn; and a surface layer comprising silicon oxide or tin oxide of 0.2 to 1,000 nm in thickness formed on the inner layer.

[0013]

The alloy preferably comprises Si or Sn and at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe.

The alloy preferably comprises at least an Si phase or an Sn phase and an alloy phase containing at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe.

[0014]

The negative electrode active material is preferably in the form of a thin film or a powder.

The negative electrode active material preferably includes an amorphous Si phase.

The present invention further relates to a non-aqueous electrolyte rechargeable battery comprising the above-described negative electrode active material.

[0015]

[Mode for Embodying the Invention]

The present invention relates to a negative electrode active material for a non-aqueous electrolyte rechargeable battery capable of adsorbing and desorbing lithium and comprises: an inner layer comprising at least one selected from the group consisting of Si, Sn, an alloy

containing Si and an alloy containing Sn; and a surface layer comprising silicon oxide or tin oxide of 0.2 to 1,000 nm in thickness formed on the inner layer.

[0016]

If the thickness of said silicon oxide or tin oxide is 1,000 nm or smaller, the reaction resistance becomes low and its increase is inhibited even if the charge and discharge are repeated. Thereby, a favorable cycle life characteristic is obtained.

On the other hand, if the thickness of said silicon oxide or tin oxide is larger than 1,000 nm, the reaction resistance becomes high due to the too-large thickness of silicon oxide or tin oxide. Accordingly, the cycle life characteristic becomes insufficient.

[0017]

As a result of a close study on high-temperature storage characteristic as another battery characteristic, it has been found that the high-temperature storage characteristic is favorable when the thickness of silicon oxide or tin oxide is 0.2 nm or larger, but deteriorated when the thickness is less than 0.2 nm. In this context, the favorable high-temperature storage characteristic means that a battery in a charged state exhibits high discharge capacity after being stored at high temperatures.

[0018]

Though the precise mechanism is unknown, it is

assumed that a side reaction between the alloy surface and the electrolyte is prone to occur in a high temperature state, and silicon oxide or tin oxide prevents the side reaction. If silicon oxide or tin oxide is too thin or does not exist, the side reaction cannot be prevented, thereby increasing the reaction resistance, decreasing the discharge capacity and deteriorating the high-temperature storage characteristic.

[0019]

Therefore, the favorable cycle life characteristic and high-temperature storage characteristic are obtained when the thickness of silicon oxide or tin oxide formed on the inner layer comprising at least one selected from the group consisting of Si, Sn, an alloy containing Si and an alloy containing Sn is 0.2 to 1,000 nm.

[0020]

It is preferable that the alloy includes Si or Sn, and at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe. With use of such an alloy, the negative electrode active material can be stabilized and prevented from pulverizing during the repeated charge and discharge. If the negative electrode active material is pulverized, the negative electrode active material decreases in reactivity and the cycle life is apt to decrease.

[0021]

Further, if the ratio of the element to be alloyed with Si or Sn increases, the capacity of the resulting alloy

decreases. Therefore, it is not preferable to use the element to be alloyed with Si or Sn in a larger ratio than is necessary.

[0022]

The alloy preferably includes at least an Si phase or an Sn phase, Si or Sn, and an alloy phase containing at least an element selected from the group consisting of Ti, Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe.

[0023]

The use of such an alloy can prevent the negative electrode active material from pulverizing during the repeated charge and discharge more effectively. Accordingly, further improvement in cycle life characteristic is expected.

[0024]

The above-described negative electrode active material may be in either form of a thin film or a powder.

The thin film may be formed by any method as long as the method forms a thin film. For example, vacuum deposition, chemical vapor deposition (CVD), sputtering, plating and the like may be employed.

[0025]

The powder may be formed by any method as long as the method gives a powder. For example, may be adopted a method of preparing an alloy mass first and then pulverizing the mass into a powder and a method of directly preparing a powder. Examples thereof include a method of preparing an

alloy mass by a melting method and then pulverizing the mass with a stamp mill or ball mill, and a method of directly obtaining a powder by atomization or mechanical alloying. Other examples of the method for preparing the alloy mass include a roll quenching method and a rotational electrode method.

[0026]

The above-described negative electrode active material preferably includes an amorphous Si phase. The amorphous Si phase is more effective in inhibiting the pulverizing of the negative electrode active material through the repeated charge and discharge than a crystalline Si phase, thereby improving the cycle life characteristic.

In this context, the amorphous Si phase means a phase in which a peak is not at a diffraction angle (2θ) attributed to the crystalline plane of the Si phase in a wide angle X-ray diffraction pattern of Si. On the other hand, the crystalline Si phase means a phase in which a peak is at a diffraction angle (2θ) attributed to the crystalline plane of the Si phase in a wide angle X-ray diffraction pattern of Si.

[0027]

[Working Examples]

Hereinafter, the present invention is explained in detail by way of Examples. However, the invention is not limited thereto.

[0028]

《Examples 1-12 and Comparative Examples 1-9》

(i) Preparation of negative electrode active material

In Examples 1-6 and Comparative Examples 1-4, alloys containing Si or Sn were synthesized in the following manner. Table 1 shows the compositions of the alloys.

First, certain elements in the form of mass, plate or particles were mixed in a given ratio, which was melted under an Ar atmosphere by high-frequency induction melting process. Then, the resulting alloy mass was pulverized with a stamp mill under the Ar atmosphere. The obtained alloy was shifted through a sieve of 45 micron mesh to obtain negative electrode active material particles having an average particle diameter of 28 μm.

[0029]

The obtained alloy powder was subjected to heat treatment at 200 °C for one hour under an atmosphere of oxygen and Ar mixed in a volume ratio of 0.5:99.5 (Examples 1 and 4).

The obtained alloy powder was subjected to heat treatment in the same manner as in Example 1 except that an atmosphere of oxygen and Ar mixed in a volume ratio of 10:90 was used (Examples 2 and 5).

The obtained alloy powder was immersed in an aqueous solution containing 0.5% by weight of hydrofluoric acid at room temperature for 5 minutes and then dried at 60 °C under vacuum (Examples 3 and 6).

[0030]

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The obtained alloy powder was subjected to heat treatment at 200 ℃ for an hour under atmospheric air (Comparative Examples 1 and 3).

The obtained alloy powder was immersed in a mixed aqueous solution containing 20% by weight of hydrofluoric acid and 20% by weight of nitric acid at room temperature for 5 minutes and then dried at 60 ℃ under vacuum (Comparative Examples 2 and 4).

[0031]

In Examples 7 to 12 and Comparative Examples 5 to 8, Si or Sn powder was treated in the following manner.

Si or Sn powder was subjected to heat treatment at 200 ℃ for an hour under an atmosphere of oxygen and Ar mixed in a volume ratio of 0.5:99.5 (Examples 7 and 10).

Si or Sn powder was subjected to heat treatment in the same manner as in Example 7 except that an atmosphere of oxygen and Ar mixed in a volume ratio of 10:90 was used (Examples 8 and 11).

Si or Sn powder was immersed in an aqueous solution containing 0.5% by weight of hydrofluoric acid at room temperature for 5 minutes and then dried at 60 ℃ under vacuum (Examples 9 and 12).

[0032]

Si or Sn powder was subjected to heat treatment at 200 ℃ for 1 hour under atmospheric air (Comparative examples 5 and 7).

Si or Sn powder was immersed in a mixed aqueous solution containing 20% by weight of hydrofluoric acid and 20% by weight of nitric acid at room temperature for 5 minutes and then dried at 60 ℃ under vacuum (Comparative Examples 6 and 8).

[0033]

(ii) Production of negative electrode

Using the negative electrode active materials formed in Examples 1-12 and Comparative Examples 1-8, negative electrodes were formed. Further, a comparative negative electrode was formed using graphite (Comparative Example 9).

Each of the negative electrode active material powders shown in Tables 1 was mixed with a carbon powder as a conductive material and PVdF as a binder in a ratio of 75:20:5 by weight to give a mixture. The mixture was dispersed in dehydrated N-methylpyrrolidinone to obtain a slurry. This slurry was applied to an electrolytic copper foil serving as a negative electrode current collector, which was dried and then rolled to give a negative electrode.

[0034]

(iii) Production of positive electrode

Lithium cobaltate ($LiCoO_2$) powder as a positive electrode active material, a carbon powder as a conductive material and PVdF as a binder were mixed in a ratio of 85:10:5 by weight to give a mixture. This mixture was dispersed in dehydrated N-methylpyrrolidinone to give a slurry. This slurry was applied to an aluminum foil serving as a positive

electrode current collector, which was dried and then rolled to give a positive electrode.

[0035]

(iv) Fabrication of non-aqueous electrolyte rechargeable battery

FIG. 1 is a schematic vertical section of a non-aqueous electrolyte rechargeable battery. The non-aqueous electrolyte rechargeable battery as shown in FIG. 1 was fabricated in the following manner.

[0036]

A positive electrode 5 and a negative electrode 6, which were obtained as described above, were stacked with a separator 7 interposed therebetween and rolled up to form an electrode assembly 4. Insulating rings 8 were attached to the top and the bottom of the electrode assembly 4, respectively. The positive electrode 5 was connected to a sealing plate 2 via a positive electrode lead 5a. The negative electrode 6 was connected to the bottom of a battery case (negative electrode can) 1 via a negative electrode lead 6a. Then, the electrode assembly 4 was placed in the battery case 1, in which a non-aqueous electrolyte was poured. The non-aqueous electrolyte used was a solvent mixture of ethylene carbonate and ethyl methyl carbonate in a volume ratio of 1:1 containing 1 mol/L of $LiPF_6$.

[0037]

Then, the battery case 1 was sealed with the sealing

plate 2 provided with an insulating packing 3. In this manner, batteries A1-A12 (using the negative electrode active materials of Examples 1-12) and batteries X1-X9 (using the negative electrode active materials of Comparative Example 1-9) were fabricated, each of which was a cylindrical sealed lithium rechargeable battery of 18 mm in diameter and 65 mm in height. The non-aqueous electrolyte rechargeable batteries were fabricated under a dry air atmosphere adjusted to have a dew point of -50 ℃ or lower.

[0038]

[Evaluations]

① Cycle life test

Each of the batteries was subjected to repeated charge/discharge cycles. The charge was performed at 0.6 A up to 4.2 V at 20 ℃ and then the discharge was performed at 0.4 A down to 2.5 V at 20 ℃. At that time, discharge capacity C1 at the first cycle and discharge capacity C2 at the 100th cycle were measured. With respect to every battery, the ratio P (%) of discharge capacity C2 to discharge capacity C1 was calculated from the formula shown below to evaluate the cycle life characteristic of the battery. The cycle life characteristic was judged as satisfactory when the value P was 85 % or higher.

$$P (\%) = (C2/C1) \times 100$$

[0039]

② Qualitative analysis and thickness measurement of silicon

oxide

Qualitative analysis of silicon oxide was conducted using XPS-7000 manufactured by Rigaku Corporation. Al-Kα was used as an X-ray source. Narrow scan measurement was conducted under the conditions of a voltage of 10 kV, a current of 10 mA, an energy range of 114 to 94 eV and a step size of 0.08 eV. Si2p was used as the measurement element.

[0040]

Further, the thickness of silicon oxide was measured in the following manner.

Silicon oxide was subjected to Ar ion etching. The thickness of silicon oxide was determined as the difference between the etch depth when a peak of silicon oxide began to appear and the etch depth when the peak disappeared. The etching was performed under the conditions of accelerated voltage of 500 V, etching angle of 90° , ion current density of 160 μA/cm^2 and the etching rate of 0.5-5 nm/minute in terms of SiO$_2$. The minimum etch depth was 0.2 nm.

[0041]

③ Measurement of internal resistance of battery

Internal resistance of the battery at a frequency of 1 kHz was measured by an A/C impedance method. The measurement was performed after discharge at the first cycle and the 100th cycle of the above-described charge/discharge cycles.

[0042]

④ High-temperature storage test

After 5 charge/discharge cycles performed in the above-mentioned manner, discharge capacity C3 at the 5th cycle was measured. Then, after the 6th cycle charge, the battery was stored in a chamber at 80 ℃ for 3 days. After the storage period, the battery was discharged at 0.4 A down to 2.5 V at 20 ℃ to obtain discharge capacity C4. The ratio Q (%) of discharge capacity C4 to discharge capacity C3 at the 5th cycle was calculated by the following formula to evaluate the high-temperature storage characteristic of the battery. The high-temperature storage characteristic was judged as satisfactory when the value Q was 85 % or higher.

Q (%) = (C4/C3) × 100

Table 1 shows the evaluation results of each test.

[0043]

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[Table 1]

Battery number	Composition	Thickness of silicon or tin oxide (nm)	Discharge capacity C1 (mAh)	Discharge capacity C2 (mAh)	Ratio P (%)	Discharge capacity C3 (mAh)	Discharge capacity C4 (mAh)	Ratio Q (%)	Battery resistance (mΩ) First cycle	Battery resistance (mΩ) 100th cycle
Ex. 1	A1	$TiSi_3$	100	2780	2634	94.7	2773	2487	89.7	40	43
Ex. 2	A2	$TiSi_3$	1000	2755	2576	93.5	2746	2526	92.0	43	47
Ex. 3	A3	$TiSi_3$	0.2	2793	2655	95.1	2786	2432	87.3	36	40
Ex. 4	A4	Ti_2Sn_3	100	2770	2619	94.5	2762	2472	89.5	41	44
Ex. 5	A5	Ti_2Sn_3	1000	2745	2561	93.3	2736	2511	91.8	44	48
Ex. 6	A6	Ti_2Sn_3	0.2	2783	2640	94.9	2776	2417	87.1	37	41
Ex. 7	A7	Si	100	2926	2508	85.7	2905	2500	86.1	42	45
Ex. 8	A8	Si	1000	2910	2488	85.5	2889	2510	86.9	45	49
Ex. 9	A9	Si	0.2	2942	2530	86.0	2921	2486	85.1	38	42
Ex. 10	A10	Sn	100	2916	2493	85.5	2895	2485	85.8	43	46
Ex. 11	A11	Sn	1000	2900	2473	85.3	2879	2495	86.7	46	50
Ex. 12	A12	Sn	0.2	2932	2515	85.8	2911	2475	85.0	39	43
Com.Ex. 1	X1	$TiSi_3$	1100	2711	1340	49.4	2642	2440	92.3	80	125
Com.Ex. 2	X2	$TiSi_3$	<0.2	2805	2682	95.6	2799	1500	53.6	35	40
Com.Ex. 3	X3	Ti_2Sn_3	1100	2701	1325	49.1	2632	2425	92.1	82	127
Com.Ex. 4	X4	Ti_2Sn_3	<0.2	2795	2667	95.4	2789	1485	53.3	37	42
Com.Ex. 5	X5	Si	1100	2895	1251	43.2	2813	2477	88.1	85	130
Com.Ex. 6	X6	Si	<0.2	2950	2614	88.6	2933	1453	49.5	37	41
Com.Ex. 7	X7	Sn	1100	2890	1243	43.0	2808	2466	87.8	86	131
Com.Ex. 8	X8	Sn	<0.2	2940	2603	88.5	2923	1429	48.9	38	42
Com.Ex. 9	X9	Graphite	–	2000	1870	93.5	1994	1800	90.3	40	43

[0044]

As Table 1 shows, the batteries A1-A12 using the negative electrode active materials of Examples 1-12 showed higher capacity than that of the battery X9 of Comparative Example 9. Further, the cycle life characteristic and the high-temperature storage characteristic of the batteries A1-A12 were as excellent as those of the battery X9.

The thickness of silicon oxide or tin oxide on the surface of the alloy powder as the negative electrode active material was 100 nm in Examples 1, 4, 7 and 10, 1,000 nm in Examples 2, 5, 8 and 11 and 0.2 nm in Examples 3, 6, 9 and 12.

[0045]

The batteries A1-A12 using these negative electrode active materials showed the ratio P of 85.3-95.1 %, indicating that these batteries were favorable in cycle life characteristic. Further, the ratio Q was 85.0-92.0 %, showing that these batteries were excellent in high-temperature storage characteristic.

[0046]

The batteries A1-A12 showed the battery resistance of 36-46 mΩ at the first cycle, which was not so high. After the 100th cycle, the increase of the battery resistance was as small as 3-4 mΩ. Accordingly, it was found that the initial reaction resistance was low when the average thickness of silicon oxide or tin oxide was 1,000 nm or smaller and the reaction resistance was prevented from increasing through the

repeated charge and discharge. Thus, satisfactory cycle life characteristic was given.

[0047]

On the other hand, in Comparative Example 1, the thickness of silicon oxide on the alloy powder surface was 1,100 nm. Further, the battery resistance at the first cycle of the battery X1 of Comparative Example 1 was 80 mΩ, which was higher than that of the batteries A1-A12 of Examples 1-12. After the 100th cycle, the battery resistance was 125 mΩ, which was higher than the initial battery resistance by 45 mΩ.

[0048]

In view of these results, it was proved that the thickness of silicon oxide larger than 1,000 nm increases the reaction resistance due to the too-large thickness, thereby increasing the battery resistance. In consequence, the ratio P was 49.4 %, leading to unsatisfactory cycle life characteristic. The batteries X3, X5 and X7 of Comparative Example 3, 5 and 7 also showed insufficient cycle life characteristic for the same reason applied to the battery X1 of Comparative Example 1.

[0049]

Regarding the battery X2 of Comparative Example 2, silicon oxide on the alloy surface was not quantitative analyzed at the etch depth of 0.2 nm, and was not quantitative analyzed at the greater depth. Therefore, the thickness of silicon oxide on the alloy surface was estimated as less than

0.2 nm or does not exist at all. Thus, the reaction resistance derived from silicon oxide was almost zero and the ratio P was 95.6%, indicating that the cycle life characteristic was excellent. However, the ratio Q was 53.6%, showing that the high-temperature storage characteristic was unsatisfactory.

[0050]

Though the precise mechanism is unknown, it is assumed that silicon oxide or tin oxide inhibits a side reaction between the alloy surface and the electrolyte, which occurs vigorously in a high temperature state. Therefore, if silicon oxide or tin oxide is too thin or does not exist, the side reaction cannot be inhibited. Accordingly, the reaction resistance increases, discharge capacity is apt to decrease and the high-temperature storage characteristic is impaired. The batteries X4, X6 and X8 of Comparative Examples 4, 6 and 8 showed unsatisfactory high-temperature storage characteristic for the same reason applied to the battery of Comparative Example 2.

[0051]

《Examples 13-34》

Alloys shown in Table 2 were prepared by combining Si and at least an element selected from the group consisting of Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe in the same manner as in Example 1 (Examples 13-23). Further, alloys shown in Table 2 were prepared by combining Sn and at least an element

selected from the group consisting of Co, Ni, Cu, Mg, Zr, V, Mo, W, Mn and Fe (Examples 24-34).

[0052]

Negative electrodes were prepared in the same manner as in Example 1 except that the above obtained alloy powders were used as the negative electrode active materials, respectively. Then, batteries A13-A34 were fabricated in the same manner as in Example 1 except that these negative electrodes were used.

The batteries A13-A34 were evaluated in the same manner as the battery A1 of Example 1. Table 2 shows the evaluation results.

[0053]

[Table 2]

	Battery number	Composition	Thickness of silicon or tin oxide (nm)	Discharge capacity C1 (mAh)	Discharge capacity C2 (mAh)	Ratio P(%)	Discharge capacity C3 (mAh)	Discharge capacity C4 (mAh)	Ratio Q(%)	Battery resistance (mΩ)	
										First cycle	100th cycle
Ex. 13	A13	$CoSi_3$	100	2780	2615	94.1	2772	2480	89.5	41	44
Ex. 14	A14	$NiSi_3$	100	2771	2609	94.2	2763	2470	89.4	41	44
Ex. 15	A15	$CuSi$	100	2766	2595	93.8	2757	2455	89.0	42	45
Ex. 16	A16	$MgSi$	100	2765	2600	94.0	2757	2461	89.3	41	44
Ex. 17	A17	$ZrSi_3$	100	2770	2609	94.2	2762	2472	89.5	41	44
Ex. 18	A18	VSi_3	100	2771	2590	93.5	2762	2470	89.4	43	46
Ex. 19	A19	$MoSi_3$	100	2778	2601	93.6	2769	2470	89.2	43	46
Ex. 20	A20	WSi_3	100	2777	2602	93.7	2768	2469	89.2	42	45
Ex. 21	A21	$MnSi_3$	100	2772	2603	93.9	2764	2468	89.3	42	45
Ex. 22	A22	$FeSi_3$	100	2773	2600	93.8	2764	2465	89.2	42	45
Ex. 23	A23	$Co_{0.5}Ni_{0.5}Si_3$	100	2772	2608	94.1	2764	2475	89.6	41	44
Ex. 24	A24	$CoSn_3$	100	2770	2605	94.0	2762	2465	89.3	42	45
Ex. 25	A25	$NiSn_3$	100	2761	2599	94.1	2753	2455	89.2	42	45
Ex. 26	A26	Cu_2Sn_3	100	2755	2585	93.8	2747	2440	88.8	43	46
Ex. 27	A27	$MgSn$	100	2755	2590	94.0	2747	2449	89.2	42	45
Ex. 28	A28	$ZrSn_3$	100	2760	2599	94.2	2752	2457	89.3	42	45
Ex. 29	A29	VSn_3	100	2761	2580	93.4	2752	2455	89.2	44	47
Ex. 30	A30	$MoSn_3$	100	2768	2591	93.6	2759	2454	88.9	44	47
Ex. 31	A31	WSn_3	100	2767	2592	93.7	2758	2453	88.9	43	46
Ex. 32	A32	$MnSn_3$	100	2762	2593	93.9	2754	2455	89.2	43	46
Ex. 33	A33	$FeSn_3$	100	2763	2590	93.7	2754	2450	89.0	43	46
Ex. 34	A34	$Co_{0.5}Ni_{0.5}Sn_3$	100	2762	2598	94.1	2754	2460	89.3	42	45

[0054]

As Table 2 shows, the batteries A13-A34 showed higher capacity than the battery X9 of Comparative Example 9. Further, the cycle life characteristic and the high-temperature storage characteristic of the batteries A13-A34 were as excellent as those of the battery X9.

As Table 2 shows, the batteries A13-A34 showed the ratio P of 93.4-94.2 %, indicating that these batteries were satisfactory in cycle life characteristic. Further, the ratio Q was 88.8-89.6 %, showing that these batteries were excellent in high-temperature storage characteristic. In these batteries, the thickness of silicon oxide or tin oxide on the alloy powder surface was 0.2-1,000 nm.

[0055]

《Examples 35-38》

Alloys having the compositions shown in Table 3 were prepared in the following manner.

First, certain elements in the form of mass, plate or particles were mixed in a given ratio, which was melted under an Ar atmosphere by high-frequency induction melting process. Then, the mixture was cooled under the Ar atmosphere by atomization to prepare spherical alloy powder as a negative electrode active material. The alloy powder was shifted through a sieve of 45 micron mesh to give alloy powders having an average particle diameter of 28 μm. These alloy powders were subjected to heat treatment under the same conditions as

in Example 1.

[0056]

According to measurement by wide angle X-ray diffraction of the resulting alloy powders, the alloy powder of Example 35 included two phases of an Si phase and a $TiSi_2$ phase, while that of Example 36 included two phases of an Sn phase and a Ti_6Sn_5 phase.

[0057]

Each negative electrode was prepared in the same manner as in Example 1 except that the alloy powders thus obtained were used as the negative electrode active material. Batteries A35-A38 were fabricated in the same manner as in Example 1 except that the obtained negative electrode was used.

The batteries were evaluated in the same manner as the battery A1 of Example 1.

Table 3 shows the evaluation results.

[0058]

[Table 3]

	Battery number	Composition	Alloy phase	Thickness of silicon or tin oxide (nm)	Discharge capacity C1 (mAh)	Discharge capacity C2 (mAh)	Ratio P(%)	Discharge capacity C3 (mAh)	Discharge capacity C4 (mAh)	Ratio Q(%)	Battery resistance (mΩ)	
											First cycle	100th cycle
Ex. 35	A35	$TiSi_3$	$Si+TiSi_2$	100	2780	2655	95.5	2774	2488	89.7	40	43
Ex. 36	A36	Ti_2Sn_3	$Sn+Ti_6Sn_5$	100	2770	2643	95.4	2764	2473	89.5	41	44
Ex. 37	A37	$TiSi_2$	$TiSi_2$	100	2605	2381	91.4	2594	2325	89.6	40	43
Ex. 38	A38	Ti_6Sn_5	Ti_6Sn_5	100	2600	2377	91.4	2589	2319	89.6	41	44

[0059]

As Table 3 shows, the batteries A37 and A38 each using the single-phase alloys of Examples 37 and 38 as the negative electrode active materials showed excellent cycle life characteristic and high-temperature storage characteristic. The batteries A35 and A36 each using the two-phase alloys of Examples 35 and 36 as the negative electrode active materials showed superior cycle life characteristic and high-temperature storage characteristic to those of the batteries A37 and A38.

[0060]

《Examples 39-45》

According to various methods as described below, thin Si films were formed.

According to vacuum deposition, an Si mass was evaporated using an electron beam under vacuum of about 0.00003 Torr to form a thin Si film on an electrolytic copper foil (Example 39).

[0061]

According to chemical vapor deposition (CVD), silane was used as a source gas and hydrogen was used as a carrier gas. Then, a thin Si film was formed on an electrolytic copper foil under vacuum of 0.3 Torr while heating the electrolytic copper foil at 200 ℃ (Example 40).

[0062]

Further, a thin Si film was formed by sputtering on

an electrolytic copper foil under vacuum of 0.1 Torr and high
frequency power of 200 W (Example 41).

The thus obtained thin Si films were subjected to
heat treatment under an atmosphere of oxygen and Ar mixed in
the volume ratio of 0.5:99.5 at 200 ℃ for an hour.

[0063]

Further, a thin TiSi$_2$ alloy film was formed by
vacuum deposition as described below (Example 43).

Masses of Si and Ti were evaporated under vacuum of
about 0.00003 Torr using an electron beam to form a thin TiSi$_2$
alloy film on an electrolytic copper foil. The thin TiSi$_2$
alloy film was subjected to heat treatment under an atmosphere
of oxygen and Ar mixed in the volume ratio of 0.5:99.5 at
200 ℃ for an hour.

[0064]

A thin Sn film was formed by electroless plating as
described below (Example 42).

A plating solution was prepared by dissolving 0.1
mol/L of SnSO$_4$ in a 0.1 mol/L H$_2$SO$_4$ aqueous solution. In 100 ml
of the plating solution, an electrolytic copper foil was
immersed at a bath temperature of 40 ℃ for 15 minutes to form
a thin Sn film thereon.

Then, the thin Sn film was subjected to heat
treatment under an atmosphere of oxygen and Ar mixed in the
volume ratio of 0.5:99.5 at 200 ℃ for an hour.

[0065]

A thin CoSn alloy film was formed by electroless plating as described below (Example 44).

A plating solution was prepared by dissolving 0.1 mol/L of $SnSO_4$ and 0.1 mol/L of $CoSO_4$ in a 0.1 mol/L H_2SO_4 aqueous solution. In 100 ml of the plating solution, an electrolytic copper foil was immersed at a bath temperature of 40 ℃ for 15 minutes.

Then, the thin alloy film was subjected to heat treatment under an atmosphere of oxygen and Ar mixed in the volume ratio of 0.5:99.5 at 200 ℃ for an hour.

[0066]

A thin film comprising a crystalline Si phase was formed in the following manner (Example 45).

A thin Si film was formed in the same manner as in Example 40, which was subjected to heat treatment under an atmosphere of oxygen and Ar mixed in the volume ratio of 0.5:99.5 at 700 ℃ for an hour. The thin Si film had a peak at a diffraction angle attributed to Si in a wide angle X-ray diffraction pattern of Si. Therefore, it was confirmed that the thin film comprises the crystalline Si.

[0067]

Each of the negative electrode active materials in the thin film form obtained in the above were used as the negative electrodes. Batteries A39-A45 were fabricated in the same manner as in Example 1 except that the thus obtained negative electrodes were used.

The batteries were evaluated in the same manner as the battery A1 of Example 1.

Table 4 shows the evaluation results.

[0068]

[Table 4]

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	Battery number	Composition	Thickness of silicon or tin oxide(nm)	Discharge capacity C1(mAh)	Discharge capacity C2(mAh)	Ratio P(%)	Discharge capacity C3(mAh)	Discharge capacity C4(mAh)	Ratio Q(%)	Battery resistance (mΩ)	
										First cycle	100th cycle
Ex. 39	A39	Si	100	2930	2670	91.1	2917	2585	88.6	42	45
Ex. 40	A40	Si	100	2932	2667	91.0	2919	2578	88.3	42	45
Ex. 41	A41	Si	100	2935	2672	91.0	2922	2590	88.6	42	45
Ex. 42	A42	Sn	100	2950	2521	85.5	2929	2506	85.6	43	46
Ex. 43	A43	TiSi$_2$	100	2600	2390	91.9	2590	2321	89.6	40	43
Ex. 44	A44	CoSn	100	2450	2214	90.4	2438	2192	89.9	41	44
Ex. 45	A45	Si	100	2930	2530	86.3	2910	2545	87.5	42	45

[0069]

As Table 4 shows, the batteries A39-A45 of Examples 39-45 showed higher capacity than the battery X9 of Comparative Example 9. Further, the cycle life characteristic and the high-temperature storage characteristic of the batteries A39-A45 were as excellent as those of the battery X9.

As Table 4 shows, the batteries A39-A45 showed the ratio P of 85.5-91.9 %, indicating that these batteries were satisfactory in cycle life characteristic. Further, the ratio Q was 85.6-89.9 %, showing that these batteries were satisfactory in high-temperature storage characteristic.

[0070]

According to wide angle X-ray diffraction measurement, the thin Si film of Example 40 had no peak at the diffraction angle attributed to Si and was found to comprise an amorphous Si phase. In comparison with the thin film of Example 45 comprising a crystalline Si phase, the battery A40 of Example 40 showed the ratio P of 91.0 %, which was higher than the ratio P of the battery A45 (86.3 %) as shown in Table 4, indicating that excellent cycle life characteristic was obtained.

It is assumed that the amorphous Si phase is more effective than the crystalline Si phase in inhibiting the pulverization of the negative electrode active material during the repeated charge and discharge.

[0071]

In the above Examples, the electrolytic copper foil was used as the copper foil. However, the present invention is not limited thereto. For example, a rolled copper foil may be used. The copper foil surface may be flat or rough.

Moreover, $LiCoO_2$ used as the positive electrode active material in Examples of the present invention may be replaced with a positive electrode capable of reversibly charging and discharging, such as $LiMn_2O_4$ and $LiNiO_2$.

[0072]

Further, the above Examples were applied to a cylindrical battery. However, the present invention is not limited to this structure and has a similar effect when it is applied to rechargeable batteries in a coin form, prismatic form and flat form.

[0073]

[Effect of the Invention]

As described above, the present invention intends to provide a negative electrode active material for a non-aqueous electrolyte rechargeable battery which adsorbs a large amount of lithium and has reduced reaction resistance. Further, with the use of the negative electrode active material, the present invention intends to provide a non-aqueous electrolyte rechargeable battery having high capacity, and excellent cycle life characteristic and high-temperature storage characteristic.

[BRIEF EXPLANATION OF THE DRAWINGS]

[FIG.1]

A schematic vertical cross section of the cylindrical battery according to Examples of the present invention.

[Explanation of Reference Numerals]

1. Battery case

2. Sealing plate

3. Insulating packing

4. Electrode assembly

5. Positive electrode

6. Negative electrode

7. Separator

5a Positive lead plate

6a Negative lead plate

8. Insulating ring

[DOCUMENT NAME] Drawing

[FIG. 1]

2003-099523

(Translation)

[DOCUMENT NAME] Abstract

[ABSTRACT]

[OBJECTIVE] To provide a non-aqueous electrolyte rechargeable battery which adsorbs a large amount of lithium and has reduced reaction resistance.

[SOLVING MEANS] The negative electrode active material for a non-aqueous electrolyte rechargeable battery capable of adsorbing and desorbing lithium includes a inner layer comprising at least one selected from the group consisting of Si, Sn, an alloy containing Si and an alloy containing Sn, and includes a surface layer comprising silicon oxide or tin oxide formed on the inner layer and has a thickness of 0.2 to 1000 nm.

[SELECTED DRAWING] None